PB82-167172

Growth Laws for the Formation of Secondary Ambient Aerosols: Implications for Chemical Conversion Mechanisms

Minnesota Univ., Minneapolis

Prepared for

Environmental Sciences Research Lab.
Research Triangle Park, NC

Jan 82

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1. REPORT NO. EPA-600/J-82-083	2. Journal Article	3. PB82-167172
4. TITLE AND SUBTITLE: GROWTH LAWS FOR THE FORMATION OF SECONDARY AMBIENT AEROSOLS: Implications for Chemical Conversion Mechanisms		5. REPORT DATE: January 1982 6. PERFORMING ORGANIZATION CODE: 054136
7. AUTHOR(S): P.H. McMurry and J.C. Wilson		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Particle Technology Laboratory Department of Mechanical Engineering 111 Church Street, SE Minneapolis, MN 55455		10. PROGRAM ELEMENT NO.: CDTA1D/02-0209 (FY-82) 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS: Environmental Scineces Research Laboratory - RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, N.C.		13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE: EPA/600/09

15. SUPPLEMENTARY NOTES: REFERENCE: Atmospheric Environment, 16(1):121-134, 1982.

16. ABSTRACT

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT: RELEASE TO PUBLIC	19. SECURITY CLASS (This Report): UNCLASSIFIED 20 SECURITY CLASS (This page): UNCLASSIFIED	21. NO. OF PAGES 22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS REPRODUCED BY

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U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

EPA-600/J-82-083
Journal Article

Atmospheric Environment Vol. 16, No. 1, pp. 121–134, 1982
Printed in Great Britain

GROWTH LAWS FOR THE FORMATION OF SECONDARY AMBIENT AEROSOLS: IMPLICATIONS FOR CHEMICAL CONVERSION MECHANISMS

P. H. McMURRY and J. C. WILSON

Particle Technology Laboratory, Department of Mechanical Engineering, 111 Church Street Southeast, Minneapolis, MN 55455, U.S.A.

(*First received* 28 *July* 1980 *and in final form* 28 *January* 1981)

Abstract—The evolution of aerosol size distributions growing by gas-to-particle conversion has been observed recently in field and laboratory studies. A technique for extracting particle diameter growth rates from such data is presented. The functional dependence of these growth rates on particle diameter (i.e. the growth law) is then examined to infer clues about possible chemical mechanisms of gas-to-particle conversion. The data are consistent with the conclusion that droplet phase (heterogeneous) reactions were important in the Great Smoky Mountains where relative humidities were high (r.h. > 75%), while gas phase reactions were the predominant mechanism in smog chamber experiments (r.h. ≃ 35%).

INTRODUCTION

Aerosols formed in the atmosphere by gas-to-particle conversion often comprise a substantial proportion of the submicron aerosol mass. These secondary aerosols are mainly composed of sulfates, nitrates and organics in various proportions and are responsible for several of the effects associated with polluted air. For example, visibility reduction resulting from light scattered by secondary aerosols has been well documented for a variety of locations including the southwestern United States (Trijonis, 1979), the eastern United States (Husar, 1979) and Los Angeles (White and Roberts, 1977; Cass, 1977). Because these particles penetrate deep into the lungs (Task Group on Lung Dynamics, 1966), it has also been hypothesized that they may be associated with increased morbidity during some air pollution episodes.

Secondary aerosols can be formed by a variety of chemical mechanisms as shown schematically in Fig. 1. For example, laboratory studies have shown that SO_2 can react in the gas phase (see reviews by Sander and Seinfeld, 1976 and Calvert *et al.*, 1978) to form low vapor pressure products which either condense on existing particles or form new particles by combining with growing molecular clusters (McMurry and Friedlander, 1979). SO_2 can also be oxidized on particle surfaces (Novokov *et al.*, 1974; Judeikis and Siegel, 1973). Several mechanisms by which dissolved SO_2 can be converted to SO_4^{2-} within airborne

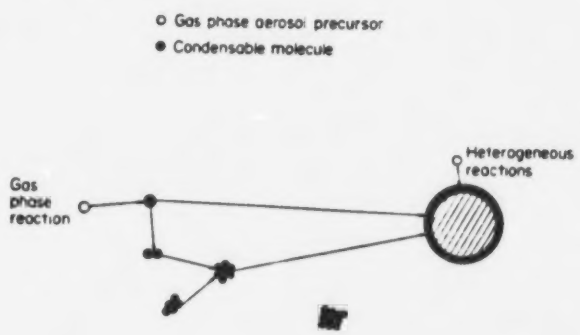

Fig. 1. A schematic diagram showing aerosol formation by different chemical mechanisms. Condensable molecules ($Dp \simeq 0.5$ nm) formed by chemical reactions involving gas phase precursors can combine with other condensable molecules or molecular clusters to form new particles, or condense on preexisting aerosol ($Dp \geq 0.01$ μm) causing them to grow. Alternatively, aerosol precursor gases can react to form secondary aerosol on the surfaces of or within existing aerosol particles.

droplets have also been proposed (e.g. Junge and Ryan, 1958; Penkett *et al.*, 1979). Chemical reactions on or within aerosol particles are classified as heterogeneous reactions. A similar list of possible conversion mechanisms will also apply for other aerosol precursors.

Current understanding of tropospheric chemistry is often inadequate to predict the predominant conversion mechanism for a given aerosol precursor in ambient air. Middleton, Kiang and Mohnen (1980) surveyed the literature for kinetic studies of SO_2 oxidation, and made estimates of the relative importances of various conversion mechanisms under varied ambient conditions. Data and measuring techniques are often not available to evaluate these predictions in the field, however. There is some evidence to show that conversion rates for SO_2 increase with increasing relative humidity (Cass, 1977; Smith and Jeffrey, 1975) which suggests that droplet phase reactions may be important at high humidities. An alternate hypothesis which is also consistent with this observation is that OH concentrations may be influenced by ambient humidity. Other studies in different environments (e.g. Husar *et al.*, 1978; Roberts and Williams, 1979; Whitby, 1979) have shown that sunlight is an important ingredient.

Information about possible chemical conversion mechanisms (e.g. surface, droplet phase or gas phase reactions) for aerosol formation in ambient air can sometimes be inferred by analyzing data for aerosol size distributions. The ideas behind this data interpretation technique were originally developed by Heisler and Friedlander (1977), who studied the growth of aerosols formed by photochemical reactions involving cyclopentene and cyclohexene in laboratory experiments. They showed that growth rates of individual particles could be calculated by analyzing the changes in aerosol size distributions measured at several times during gas-to-particle conversion. By calculating growth rates for particles of different sizes, the functional dependence of particle diameter growth rate on particle diameter can be determined. These experimental results can then be compared with theoretical expressions relating particle diameter growth rates to particle diameter (i.e. growth laws). Theory predicts different growth laws for different chemical mechanisms of aerosol formation. By matching data with consistent growth laws, it is possible to find chemical mechanisms which are consistent with the data, as well as to exclude inconsistent mechanisms.

In this paper, the techniques outlined above have been applied to ambient and smog chamber data. It has been found that sulfate aerosol formation observed in the Great Smoky Mountains at high relative humidities was consistent with droplet phase reactions, while sulfate aerosol formation in smog chamber experiments at low humidity was consistent with condensation of products formed by gas phase reactions. Data obtained in the St. Louis urban plume are consistent with simultaneous gas phase and droplet phase reactions. These results help explain differences in aerosol size distributions observed under varied meteorological and geographical conditions. In addition, this paper provides information about chemical mechanisms of secondary aerosol formation in ambient air which generally cannot be obtained by direct chemical measurements.

THEORY

The aerosol size distribution function $n(D_p, \mathbf{r}, t)$ is defined such that $n(D_p, \mathbf{r}, t)\,dD_p$ equals the number concentration of particles in the infinitesimal size interval D_p to $D_p + dD_p$ at spatial position $\mathbf{r}$ and time t. Aerosol size distributions in ambient air can change by many processes. For example, if the aerosol is not spatially homogeneous, the size distribution at $\mathbf{r}$ will change as a result of convective transport or Brownian diffusion. Coagulation, gas-to-particle conversion and gravitational settling are other processes which may cause the aerosol size distribution to change with time. The general equation which gives the rate of change of the aerosol size distribution by these processes is (Friedlander, 1977)

$$\frac{\partial n}{\partial t} = \underbrace{-\nabla\cdot\mathbf{v}n}_{\substack{\text{convection}\\ \text{transport}}} + \underbrace{D\nabla^2 n}_{\substack{\text{Brownian}\\ \text{Diffusion}}} + \underbrace{\left(\frac{\partial n}{\partial t}\right)_{\text{coag}}}_{\text{coagulation}} + \underbrace{\left(\frac{\partial n}{\partial t}\right)_{\text{growth}}}_{\substack{\text{gas-to-particle}\\ \text{conversion}}} \underbrace{-\nabla\cdot\mathbf{c}n}_{\text{settling}} \qquad (1)$$

where

$n = n(D_p, \mathbf{r}, t)$ = aerosol size distribution function,
t = time,
$\mathbf{v}$ = wind velocity,
D = particle diffusion coefficient and
$\mathbf{c}$ = gravitational settling velocity.

In this paper attention is limited to spatially homogeneous aerosols, so that transport and Brownian diffusion can be neglected. The validity of this assumption is discussed below for each of the data sets analyzed. For the particle sizes of interest (0.03–1 μm), gravitational settling and deposition by impaction or Brownian diffusion on surfaces are slow (McMahon and Denison, 1979) and can also be neglected. Thus, attention is restricted to aerosols whose size distributions change only by gas-to-particle conversion and coagulation. New particle formation, which frequently accompanies gas-to-particle conversion, is accounted for in the analysis.

In the following sections, data interpretation techniques for extracting particle diameter growth rates from aerosol size distribution data are presented. Several model growth laws for different chemical mechanisms of aerosol formation are then discussed.

These concepts are applied to analysis and interpretation of data from the experimental section.

Calculating particle diameter growth rates

Under certain conditions, particle diameter growth rates, dD_p/dt, can be calculated from the rate at which $N_s(D_p, t)$ (the concentration of particles having diameter larger than D_p) increases with time. This calculation is possible provided that changes in $N_s(D_p, t)$ are dominated by growth of particles past size D_p by gas-to-particle conversion. Other processes which might affect $N_s(D_p, t)$ are coagulation and primary aerosol emission. $N_s(D_p, t)$ can increase if two particles smaller than size D_p coagulate to form a particle larger than D_p, and can decrease if two particles larger than size D_p coagulate. Local sources of primary aerosol (e.g. soil dust or automobile tailpipe emissions) may also contribute to increases in $N_s(D_p, t)$. Calculations of dD_p/dt presented below were done for cases in which primary aerosol and coagulation were unimportant in the size ranges considered (i.e. 0.03–1.0 μm in the smog chamber and urban plume, and 0.075–1.0 μm in the Great Smoky Mountains). In addition, local emissions of soil dust dominated number concentrations of particles larger than 1.0 μm. This precluded the application of these techniques to particles larger than 1.0 μm. Soil dust emissions did not affect growth rate calculations for submicron aerosols, however, since the number concentration of aerosols larger than 1.0 μm was small compared with submicron concentrations. New particle formation may increase the concentration of particles smaller than D_p; however, growth of these new particles past size D_p is treated in the same manner as growth of preexisting particles.

For aerosols satisfying the above conditions, particle diameter growth rates can be obtained graphically. When gas-to-particle conversion is the only significant process affecting particles larger than size D_p in an aerosol, the concentration of particles larger than this size, $N_s(D_p)$, increases monotonically with time. This is illustrated by data shown in Figs 2 and 3, which have been analyzed for diameter growth rates later in this paper. If there is a unique relationship between particle growth rates and particle size, then the total concentration of particles larger than a particular growing particle remains constant. It follows that the change in diameter, ΔD_p, for such a particle during a given time interval ($\Delta t = t_2 - t_1$) can be estimated graphically, as illustrated in Fig. 3. This diameter change equals the horizontal distance between curves for $N_s(t_2)$ and $N_s(t_1)$. This diameter change can be determined for particles of arbitrary initial size. The diameter growth rate can then be calculated by dividing the diameter change, ΔD_p, by the time interval between size distribution measurements, $t_2 - t_1$. The precision with which such diameter growth

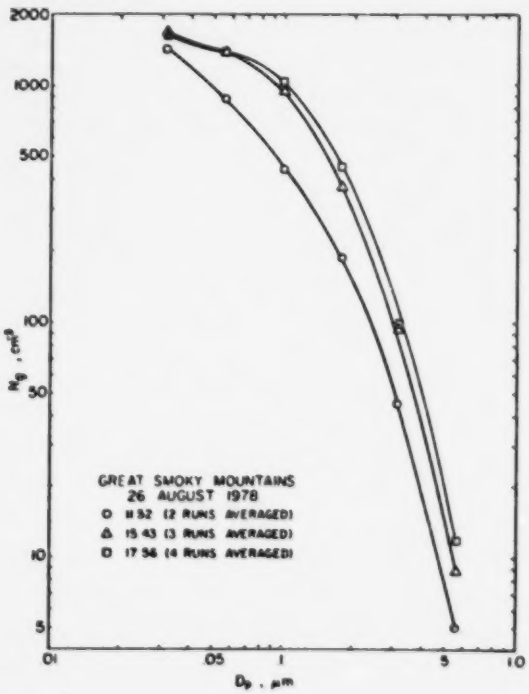

Fig. 2. The concentration of particles larger than size D_p, $N_s(D_p, t)$ as a function of particle diameter for data measured at several times in the Great Smoky Mountains.

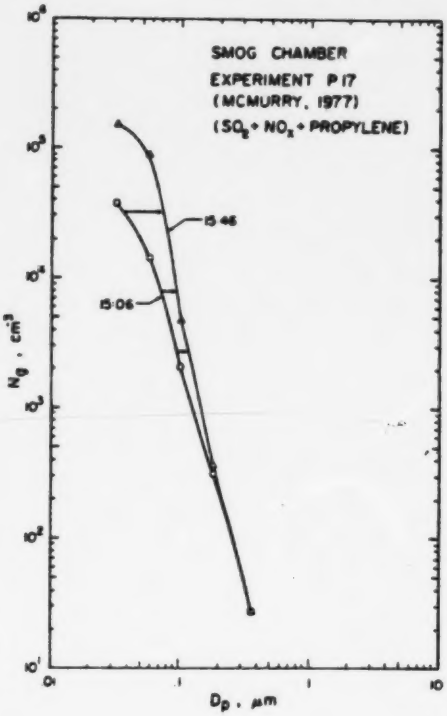

Fig. 3. The concentration of particles larger than size D_p, $N_g(D_p)$, as a function of particle diameter for smog chamber aerosols measured at several times during gas-to-particle conversion. Note that growth of particles larger than 0.2 μm was not observed. The arrows represent diameter changes for particles of several different initial sizes.

rates can be calculated is limited by the precision with which aerosol size distributions can be measured and by the extent of growth during the time interval between measurements.

In this paper, diameter growth rates have been calculated analytically rather than graphically. This analytical approach allows estimation of the uncertainty in particle diameter growth rates and eliminates the need for arbitrary interpolations when plotting curves of $N_g(D_p, t)$ vs D_p. This analytical result can be derived by examining the growth term in equation (1). This growth term may be expressed in terms of the particle current I, where I is the number of particles per unit time, per unit volume of gas which grow past diameter D_p (Friedlander, 1977). This definition implies equation (2).

$$\left.\frac{\partial n}{\partial t}\right)_{\text{growth}} = -\frac{\partial I}{\partial D_p} \tag{2}$$

If all particles of diameter D_p grow by dD_p in a time interval, dt, then the particle current can be written as follows:

$$I(D_p, t) = n(D_p, t)\frac{dD_p}{dt}. \tag{3}$$

Combining the non-zero terms from Equation (1) with Equations (2) and (3) results in an equation for n in terms of the particle growth rate.

$$\frac{\partial n}{\partial t} = -\frac{\partial}{\partial D_p}\left[n(D_p, t)\frac{dD_p}{dt}\right] \tag{4}$$

Equation (4) can be integrated with respect to D_p from D_p, a lower boundary, to infinity. The result is

$$\frac{\partial}{\partial t}N_g(D_p, t) = n(D_p, t)\frac{dD_p}{dt}, \tag{5}$$

where $N_g(D_p)$ is equal to the number of particles per cm^3 larger than D_p. The particle current, I, is zero for $D_p = \infty$.

In practice, successive measurements of N_g are separated by significant time intervals. Therefore, Equation (5) is integrated from the time of the first measurement, t_1, to the time of the next, t_2, assuming dD_p/dt to be constant during this time interval. The average value for particle diameter growth rates is then given by

$$\frac{dD_p}{dt} = \frac{N_g(D_p, t_2) - N_g(D_p, t_1)}{(t_2 - t_1)n_{av}(D_p)}. \tag{6}$$

where

$$n_{av}(D_p) = [n(D_p, t_1) + n(D_p, t_2)]/2.$$

With Equation (6) particle diameter growth rates can be calculated from size distribution measurements of a growing aerosol. As shown above, Equation (6) applies in cases where the aerosol is spatially homogeneous within the air mass being sampled so that $n(D_p, t)$ is not changed by convection, where losses by diffusion and sedimentation are negligible, and where changes due to gas-to-particle conversion dominate those due to coagulation. In addition, at each instant of time, particle growth rates must be a unique function of particle diameter.

Model growth laws

The chemical mechanisms of aerosol formation may impose on the growing aerosol a specific functional relationship between $\frac{dD_p}{dt}$ and D_p. Theoretical expressions which give the dependence of $\frac{dD_p}{dt}$ upon D_p are called growth laws (Friedlander, 1977). In this section several mechanisms which may be important in secondary aerosol formation are discussed and the model growth laws following from each are presented in Table 1 and are illustrated graphically in Fig. 4. The diameter dependencies of both particle volume growth rates (dv/dt) and particle diameter growth rates are indicated in the table. The time dependence of the particle growth rates is independent of particle size for these mechanisms, and has been omitted.

If aerosol growth results from condensation of low vapor pressure products formed by gas phase

Table 1. Some simple theoretical growth laws

Mechanism controlled by:	Volume growth rate	Diameter growth rate
Diffusion in gas phase of products of a gas phase reaction:		
Free molecule regime $D_p \ll$ Mean free path	$\frac{dv}{dt} \propto D_p^2$	$\frac{dD_p}{dt} \propto D_p^0$
Continuum regime $D_p \gg$ Mean free path	$\frac{dv}{dt} \propto D_p$	$\frac{dD_p}{dt} \propto D_p^{-1}$
Transition regime ($D_p \sim$ Mean free path)*	$\frac{dv}{dt} \propto D_p\left(\frac{1.51 + 2.08\,\mathrm{Kn}}{1.51 + \mathrm{Kn}(1.08 + 6.04\beta) + 8.32\beta\,\mathrm{Kn}^2}\right)$	$\frac{dD_p}{dt} \propto \frac{1}{D_p}\left(\frac{1.51 + 2.08\,\mathrm{Kn}}{1.51 + \mathrm{Kn}(1.08 + 6.04\beta) + 8.32\beta\,\mathrm{Kn}^2}\right)$
Surface reaction:	$\frac{dv}{dt} \propto D_p^2$	$\frac{dD_p}{dt} \propto D_p^0$
Volume reaction:	$\frac{dv}{dt} \propto D_p^3$	$\frac{dD_p}{dt} \propto D_p^{+1}$

* From Bademosi and Liu (1971). Kn is particle Knudsen No. (= Mean free path/radius), and β is a proportionally constant between diffusion constant and mean free path for condensing molecules. The reader is referred to Davis and Ray (1978) for a discussion regarding the application of this semi-theoretical result.

reactions, particle growth rates are limited by condensation rates. Condensation theory shows (e.g. Friedlander, 1977) that volume growth rates (dv/dt) for particles much smaller than the mean free path of air should be proportional to particle surface area ($\propto D_p^2$), while for particles in the continuum regime ($D_p \gg$ mean free path), dv/dt is proportional to particle diameter. A growth law for the condensational growth of transition regime aerosols ($D_p \simeq$ mean free path) based on the work of Bademosi and Liu (1971) is also shown in Table 1. The reader is referred to Davis and Ray (1978) for a summary of transition regime condensation formulae. The formation of H_2SO_4 in the gas phase by free radical oxidation of SO_2 is one mechanism expected to produce aerosol growth obeying these condensation-controlled growth laws.

If chemical reactions leading to secondary aerosol formation take place on particle surfaces, the volume growth rate of a particle may be proportional to particle surface area ($dv/dt \propto D_p^2$). This will be true provided that rates of reaction on particle surfaces are slow compared with rates of transport of reactant gases to the particle surface. Calculated collision rates between typical concentrations of known aerosol precursor gases (e.g. SO_2) and particles are generally greatly in excess of rates of gas-to-particle conversion, so a surface limited volume growth rate is plausible for this mechanism.

At high humidities, aerosol particles often deliquesce to form droplets. In this case, aerosol precursor gases can dissolve in the droplets and react to form secondary aerosol. If such liquid phase reactions occur at a uniform rate throughout the droplet volumes, the rate of particle volume growth will be proportional to particle volume. Liquid phase reactions which occur quickly compared to the transport of dissolved precursor gas in the droplet will result in a growth law resembling that of a surface reaction.

The growth of an actual aerosol could result from a combination of chemical conversion mechanisms. In this case, the growth law might be a sum of growth laws for each mechanism, as is shown, for example, in Fig. 4(d). It is also possible that complicating factors must sometimes be considered in deriving the theoretical growth law. For example, Heisler and Friedlander (1977) found that it was necessary to account for the increased vapor pressure due to particle curvature (the Kelvin effect) in order to explain the condensational growth of particles resulting from photochemical reactions involving cyclohexene and cyclopentene. In the analysis which is presented below, however, experimental results for dD_p/dt vs D_p obtained with Equation (6) are compared only with model growth laws shown in Fig. 4. Agreement between data and a model growth law shows that the data are consistent with the indicated conversion mechanism, but does not rule out the possibility that different chemical mechanisms with similar growth laws might be occurring.

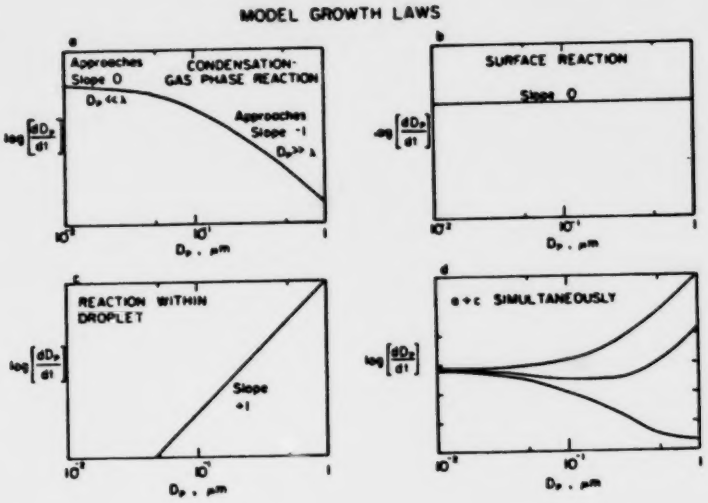

Fig. 4. Log plot showing the diameter dependence of particle diameter growth rates for several chemical conversion mechanisms. The curves in Fig. 2(d) represent growth laws which might be observed if aerosol growth by condensation and droplet phase reactions were occurring simultaneously. The three lines represent different relative rates of these processes.

EXPERIMENTS

While gas-to-particle conversion has often been observed in ambient air, complicating factors such as proximity of local primary particle emissions, transport, and dilution typically violate the assumptions made in deriving Equation (6). Therefore, there are few sets of ambient data which can be analized using this equation. Ambient air data obtained in the Great Smoky Mountains and in the St. Louis urban plume meet the required criteria and have been analyzed here. These data are supplemented by laboratory smog chamber data. A summary of supplementary information for each data set is given in Table 2. Size distributions from the Great Smoky Mountains and the St. Louis urban plume are shown in Table 3.

Uncertainties in particle diameter growth rates from Equation (6) are determined by experimental uncertainties in $N_g(D_p)$ and $n_{sv}(D_p)$. When these uncertainties are known, the uncertainty in dD_p/dt can be estimated by calculating the root mean square of the terms of the total differential of dD_p/dt. In this study, two techniques were used for estimating uncertainties in experimental data. For the St. Louis urban plume data, five size distributions were averaged for each plume cross section, and the experimental uncertainty in a given size interval was taken to be the standard deviation from the mean. These standard deviations were typically 30% and probably reflect inhomogeneities in the spatial distribution of the aerosol more than instrumental precision. For the Great Smoky Mountain data and the smog chamber data, insufficient data were available to perform this averaging process. In these cases, the uncertainty in a given size range was assumed to be 15%, reflecting the precision which has been reported for such instrumentation (Kapadia, 1980). These aerosols were spatially more uniform than the St. Louis urban plume aerosol, and where successive measurements are available they are almost always within 15%. Systematic errors leading to errors in the absolute accuracy of size distributions are poorly understood and have not been incorporated when evaluating uncertainities in dD_p/dt.

The Great Smoky Mountains

Aerosol growth was measured near Elkmont, Tennessee, in the Great Smoky Mountains National Park on 26 and 27 August, 1978. Measurements were made on the University of Minnesota Mobile Laboratory (UMML) using the instruments listed in Table 4. Size distributions were measured with an Electrical Aerosol Analyzer (EAA) and optical particle counter (OPC). The EAA raw data were converted to size distributions using a Simplex data reduction technique (Kapadia, 1980) which takes into account the non-diagonal nature of the EAA response matrix. The OPC data were used in the diameter range from 0.562 to 1.0 μm since the resolution and precision of the EAA decrease in this range. The response of the sulfate instrument used in this study (Kittelson *et al.*, 1978) depends strongly upon the ambient SO_2 level and chemical species of sulfate aerosol. Other investigators (Stevens *et al.*, 1980) have reported measuring significant sulfate aerosol in the Smoky Mountains typically in the form of H_2SO_4 partially neutralized by NH_3. SO_2 levels in the present study were below a few ppb. Therefore, the sulfate instrument was calibrated with $(NH_4)_2SO_4$ in the absence of SO_2. The instru-

Table 2. Supplementary data measured during aerosol formation episodes*

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Location	Date	Time interval	r.h.	SO_2 ppb	O_3 ppb	NO_x ppb	T °C	Dew point °C	Submicron aerosol volume $\mu m^3/cm^3$	b_{sp}, 10^{-4} m^{-1}
Great Smoky Mountains	26 Aug. 1978	1000–1700	95–65	< 5 ppb	20–40	Not available	20–29	20–22	4–10	0.25–0.7
Great Smoky Mountains	27 Aug. 1978	0900–1400	85–65	< 5 ppb	20–60	Not available	19–28	20–22	9–18	0.7–1.1
Caltech, Pasadena, CA Smog chamber	25 Aug. 1976	1506–1546	34	79–74	220–930	260 (Initially)	37	16	15–38	0.93
St. Louis urban plume	18 July 1975	0915–1200	78–83	6–16	60–120	50–86	23–27	19–22	9–16	2.3–2.9

* When a range of concentrations is given, data are ordered to show values at beginning and end of indicated time interval.

Table 3. Arithmetic mean size distributions used in aerosol growth analysis

Location	Great Smoky Mountains				St. Louis urban plume	
Date	8/26/78	8/26/78	8/27/78	8/27/78	7/18/75	7/18/75
Time	11.52	17.56	09.51	13.29	09.15	12.40
Number of distributions averaged	2	4	2	2	5	5
EAA Data D_p, μm	Number concentration in size range (cm^{-3})					
0.0316					11,566	
0.0562	546	272			2561	
0.1	447	331	497	163	1153	6070
0.178	259	586	492	365	922	2086
0.316	140	358	247	290	357	586
0.562	41	88	91	143	55.5	91
1.0	10	12	30	49	8.3	11.4
OPC data D_p, μm						
0.562	5.0	11.4	13.6	24	Not available	Not available
1.0						

Table 4. Smoky Mountain haze measurements

Variable	Instrument
Aerosol size distribution $D_p = 0.01$–$38\ \mu m$	Electrical Aerosol Analyzer (0.01–0.56 μm) (TSI, Inc. EAA Model 3030)
	Optical Particle Counters
	Modified Royco 220 (0.56–6 μm)
	Modified Royco 245 (5.6–38 μm)
Aitken nuclei concentration	Condensation Nuclei Counter (GE-1)
Aerosol light scattering coefficient (b_s)	Integrating Nephelometer (Modified MRI, Inc., Model 1561)
Aerosol sulfate and SO_2	Meloy SA 285 with Pulsed Electrostatic Precipitator (Kittelson *et al.*, 1978)
Wind speed (WSPD) and wind direction (WDIR)	Wind Indicator (MRI, Inc. Model 1074)
Ambient temperature (TO)	Aspirated Temperature Sensor (MRI, Inc. Model 840)
Dew point (TDP)	Hygrometer (EG and G, Inc. Model 880)

ment is not optimal for such low concentrations of SO_2 and it is difficult to estimate the uncertainty associated with the sulfate measurements.

Rain fell on the night of 25 August, and on the next morning the air was relatively free of haze. The cloud cover broke up after noon on 26 August with mostly clear sky observed at 1500. Winds were nearly calm throughout the two days. On 26 August, most measurements were made with the UMML stationary. Due to the lack of wind, exhaust from the generators occasionally contaminated the samples drawn from the front of the UMML. The contaminated samples contained excess fine particles and were generally discarded. Measurements from some marginally contaminated samples taken on 26 August are reported since the size distributions were unaffected at the larger diameters of interest in the analysis. On 27 August, most measurements were taken on little-traveled roads with the UMML in motion, and the problem of contamination was greatly reduced. The relative humidity varied from approx. 65 to 95% on both days with lower values being observed in the afternoons. This suggests that growth at constant humidity would have exceeded the observed growth.

Figure 5 shows the volume concentration of submicron aerosol, V –, and the aerosol light scattering coefficient, b_s, as functions of time on 26 and 27 August. Note that these parameters increased with time on both days, but did not increase throughout the night. In addition, the concentration of sulfate aerosol, expressed as $\mu g\ m^{-3}$ of SO_4^{2-}, increased during the day on the 27th. Increasing levels of aerosol sulfate were also indicated on the 26th during the day, but most readings were below the calibrated range of the instrument and are not plotted. In spite of large uncertainties, the sulfate measurements imply that

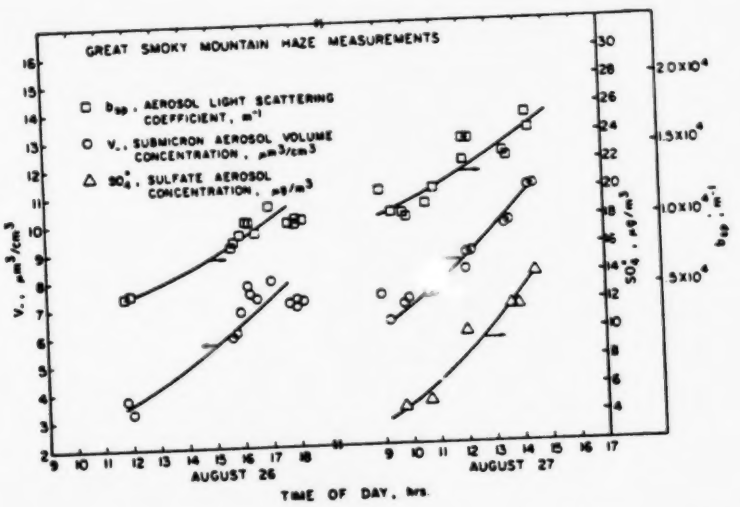
GREAT SMOKY MOUNTAIN HAZE MEASUREMENTS
□ b_{sp}, AEROSOL LIGHT SCATTERING COEFFICIENT, m^{-1}
○ V-, SUBMICRON AEROSOL VOLUME CONCENTRATION, $\mu m^3/cm^3$
△ $SO_4^=$, SULFATE AEROSOL CONCENTRATION, $\mu g/m^3$
AUGUST 26
AUGUST 27
TIME OF DAY, hrs.

Fig. 5. Submicron aerosol volume, aerosol light scattering coefficient, b_s, and aerosol sulfate concentrations as functions of time on 26 and 27 August, 1978. Note that these parameters increased steadily with time during the days but did not apparently change during the night.

significant sulfate formation did occur and that it may account for most or all of the gas-to-particle conversion.

The number concentration of aerosol particles with diameter larger than 0.01 μm remained essentially steady during the two days. On the second day the average number concentration was 1730 particles cm^{-3} with a standard deviation of 340. On the first day the measured average was higher due to the above mentioned contamination but several values fell within the range observed on the 27th. These observations suggest that the observed increases in aerosol volume and sulfate were due to growth of existing particles and that new particle formation was not important. Aerosol volume distributions measured during this episode are shown in Fig. 4. Note that new volume accumulated in particles up to 1.0 μm in dia.

In order to correctly apply Equation (6) to the data, it is necessary that the non-growth terms in Equation (1) are negligible. The transport term vanishes if the aerosol is homogeneous throughout the air mass being sampled. Calculations of air parcel trajectories indicate that the air arriving at the site at 1200 on 27 August was within 150 km of the site at the beginning of the episode on 0900 26 August. Most parcels arriving during the study were typically less than 80 km from the site at the start of the episode. The assumption that the haze aerosol was uniform within this range is unverifiable, but not unreasonable, since regional scale hazes are common in the area. Thus, we assume the haze to have been uniform over 150 km and neglect the transport term. Calculations of the coagulation rates indicate that coagulation is negligible in comparison with the growth term.

Equation 6 was applied to the size distributions in Table 3 to produce the diameter growth rates shown in Figs 7 and 8. (If the EAA data were to be used in the 0.56–1.0 μm dia. range, the 0.56 μm point on Fig. 7 would be reduced by a factor of five but the other points on Figs 7 and 8 would not be significantly altered.) These results have been compared with the theoretical growth laws of Fig. 4. Data for 26 August were qualitatively consistent with a surface limited growth law, while data from 27 August are consistent with a volume limited reaction rate. The theoretical growth law curves shown in Figs 7 and 8 represent least squares best fits of the theory to the data.

The data shown in Figs 7 and 8 are consistent with the conclusion that growth was caused by reactions on or within existing aerosol particles and not by condensation of low vapor pressure species formed in the gas phase. This conclusion is reinforced by the fact that new particle formation was judged not to be important during these measurements.

Although the data from 26 August are consistent with a surface limited growth law, it seems likely that solution phase chemical reactions and not surface reactions were predominant. Solution phase reactions could cause particle growth consistent with a surface limited growth law if reaction rates within the particle are fast compared with rates of diffusion of dissolved aerosol precursor gases from particle surfaces to the interior. Alternatively, if growth were occuring in a film of liquid surrounding an insoluble core, solution phase reactions could appear to be surface limited. It is not likely that surface reactions would appear to be volume limited, as shown by data in Fig. 8. Furthermore, during the time of these measurements, individual particles typically grew by a factor of five in volume. This insured that particle surfaces had the same

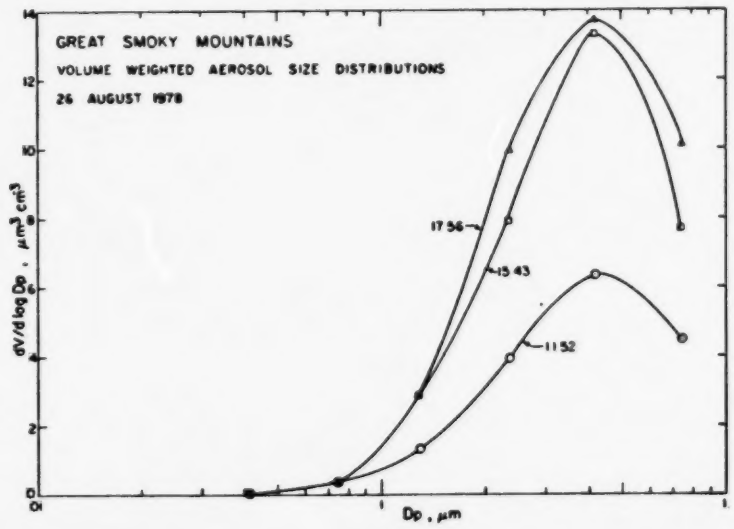

Fig. 6. Aerosol volume distributions measured in the Great Smoky Mountains on 26 August 1978. Note that a considerable amount of secondary aerosol appeared in the 0.5–1.0 μm size range where condensational growth is not expected.

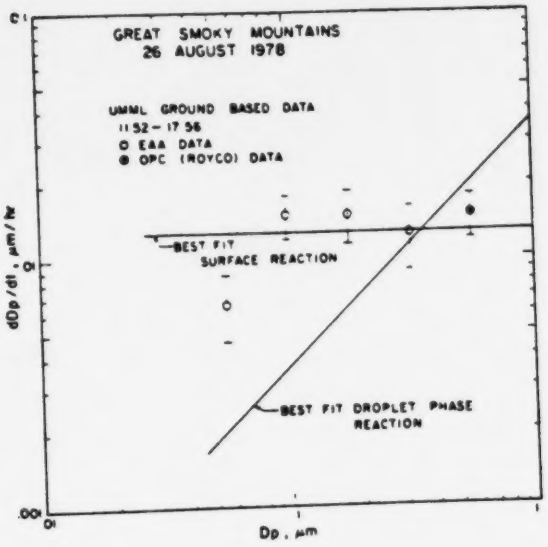

Fig. 7. Particle diameter growth rates as a function of particle diameter for aerosol data measured on 26 August, 1978 in the Great Smoky Mountains. Least squares best fit growth laws for surface and droplet phase reactions are shown. These data are consistent with surface limited growth.

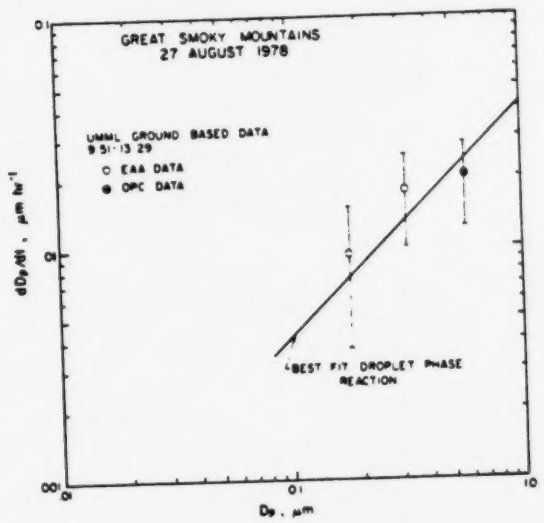

Fig. 8. Particle diameter growth rates as a function of particle diameter for size distributions measured in the Great Smoky Mountains on 27 August, 1978. The data show that growth rates tend to increase with particle diameter, in qualitative agreement with the theoretical growth law for droplet phase reactions. The solid line of slope 1 represents the least squares best fit growth law for droplet phase reactions.

chemical composition as the secondary aerosol, and were not characteristic of surfaces for primary nuclei. It is unlikely that such secondary aerosol species would provide effective sites for surface reactions.

Smog chamber experiments: $SO_2 + NO_x$ + propylene

McMurry and Friedlander (1979) reported on experiments for aerosol growth by photochemical reactions in the $SO_2 + NO_x$ + propylene system. In these experiments, a large (65 m^3), collapsible teflon bag was filled with unfiltered ambient air. When the reactants were added to this air and exposed to sunlight, the formation of secondary aerosol was initiated. Growth of the preexisting particles as well as new particle formation was observed. Size distributions were measured as functions of time with an electrical aerosol analyzer (TSI Model 3030) and with a Climet optical particle counter. The techniques discussed by Kapadia (1980) were used when reducing the electrical aerosol analyzer data. These techniques account for the non-diagonal nature of the electrical aerosol analyzer response matrix (Liu and Pui, 1975).

Data from experiment P 17 of the above study were analyzed with Equation (6) to determine the diameter dependence of particle diameter growth rates. Rates of particle losses on the reactor walls were reported by McMurry (1977), and have been accounted for. Experimental results for particle diameter growth rates in experiment P 17 are shown in Fig. 9. Only growth rates of particles equal to or larger than 0.0316 μm are shown, since coagulation was an important factor for smaller particles during the indicated time interval. Significantly, growth of particles larger than 0.2 μm was not detected.

The diameter dependence of particle growth rates in this smog chamber experiment (which is typical of particle growth resulting from SO_2 photooxidation in smog chambers) is strikingly different from that found in ambient air in the Great Smokies (Fig. 8). In the smog chamber, particle diameter growth rates decreased rapidly with increasing diameter, while in the Smokies, growth rates increased with increasing diameter. This observation is consistent with data for volume mean particle diameters which are much larger (0.4–0.5 μm) in the Smokies than in smog chamber aerosols (0.1–0.2 μm).

The smog chamber data in Fig. 9 do not agree within estimated experimental error with any of the model growth laws shown in Fig. 4. The decrease in particle growth rates with particle diameter, however, is qualitatively consistent with aerosol growth by condensation. It is possible that experimental uncertainties were underestimated.

The St. Louis urban plume

During the summer of 1975, the Environmental Protection Agency sponsored the MISTT (Midwest Interstate Sulfur Transformation and Transport) project. Part of this project included characterization of secondary aerosol formation in the St. Louis urban plume. Several analyses of these data have been presented by other investigators including White *et al.* (1976) and Whitby (1979). Data obtained on 18 July, 1975 were particularly interesting, since the aerosol size distribution downwind from the city was well characterized for several downwind distances as the day progressed.

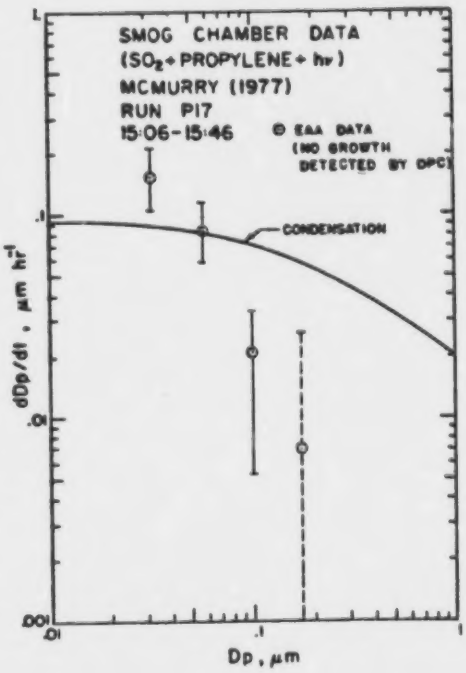

Fig. 9. Particle diameter growth rates as a function of particle diameter for size distributions measured in smog chamber reactions reported by McMurry (1977). Note that in this case, particle diameter growth rates decreased with increasing particle diameter, in contrast with the data from the Great Smoky Mountains shown in Fig. 6. Significantly, growth of particles larger than 0.2 μm was not detected with an optical particle counter. The solid line represents the least squares best fit growth law for condensational growth. Although the theory and experiment do not agree within estimated experimental error, qualitative trends are similar. It is possible that experimental errors were underestimated.

Using data acquired with an instrumented aircraft operated by Meteorology Research Incorporated, aerosol growth between 28 km (0915) and 66 km (1240) downwind of St. Louis have been analyzed. In this case, transport was clearly important. Because the aircraft moved downwind with the plume however, measurements were made in approximately the same parcel of air at the two cross sections. In addition, due to the large cross sectional area of the plume, dilution was relatively unimportant during transport between these two downwind distances; Whitby (1979) has estimated a dilution of roughly 30%. The effect of this dilution on the aerosol size distribution was not significant in

comparison with the change in the distribution due to gas-to-particle conversion and as an approximation has been ignored in the analysis. Also, calculations of particle coagulation rates indicate that gas-to-particle conversion dominated aerosol dynamics for particles equal to or larger than 0.0316 μm during the time interval of interest.

Approximately 15 size distributions were measured in the plume at each of the downwind distances. The aerosol was found to be somewhat inhomogeneous, as might be expected near a large urban source. The characteristic average plume size distribution for each cross section was obtained by averaging the five distributions which were closest to the overall average for all 15 distributions. This eliminated extreme distributions which might have been measured just outside the plume or near local downwind sources. Based on these averages, the mean submicron aerosol volume increased from 9.3 to 15.7 $\mu m^3\,cm^{-3}$ and the standard deviation for number concentration in a given size range was typically 20–30%. In this case, useful data were obtained only with an electrical aerosol analyzer (TSI Model 3030). The electrical aerosol analyzer data were again corrected to account for the non-diagonal response matrix.

Particle diameter growth rates in this urban plume between 28 and 66 km downwind are shown as a function of particle diameter in Fig. 10. Note that for large particles ($D_p > 0.2\,\mu m$), diameter growth rates tend to increase with particle diameter, while for smaller particles diameter growth rates tend to decrease with increasing diameter. This suggests that for large particles aerosol formation was dominated by a mechanism similar to that which was observed in the Great Smoky Mountains, while growth of smaller particles was qualitatively consistent with the growth of smog chamber particles.

The data shown in Fig. 10 can be explained well within experimental uncertainty by a growth law of the form

$$\frac{dD_p}{dt} = a\frac{dD_p}{dt}\Big)_{\text{condensation}} + b\frac{dD_p}{dt}\Big)_{\text{droplet phase reaction}} \quad (7)$$

Several growth laws of this form for values of a and b in various proportions are shown in Fig. 4(d). The theoretical growth law shown in Fig. 10 was obtained by using the method of least squares to find the best values of a and b for fitting a theoretical curve of this form to the data. Based on the least squares values of a and b, it was determined by integration over the size distribution that in this case, 25% of the secondary aerosol volume formation was due to droplet phase reactions, while 75% was due to condensation of products formed by gas phase reactions.

SUMMARY AND CONCLUSIONS

Aerosol growth by gas-to-particle conversion in both ambient air and in laboratory studies was analyzed to determine the diameter dependence of particle diameter growth rates. These data were then matched with theoretical growth laws to infer possible chemical mechanisms of secondary aerosol formation. Results

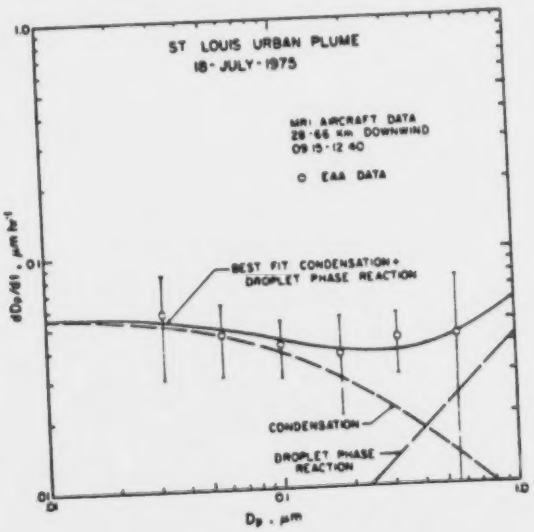

Fig. 10. Particle diameter growth rates from data obtained with an instrumented aircraft in the St. Louis urban plume during the MISTT project in July, 1975. In this case, all growth rates are based on data from an electrical aerosol analyzer. The solid line through the data points represents the least squares best fit growth law for simultaneous condensational growth and droplet phase reactions.

of this analysis have shown that aerosol formation in the Great Smoky Mountains on two humid days (r.h. $\simeq$ 65–95%) was consistent with growth by droplet phase (heterogeneous) chemical reactions. Growth of smog chamber aerosols at low relative humidities (r.h. $\simeq$ 30%) was qualitatively consistent with the assumption of growth resulting from condensation of low vapor pressure species formed by gas phase reactions. In the St. Louis urban plume, (r.h. 48–83%), it was concluded that 75% of the secondary aerosol volume formation was due to condensation, while 25% was due to droplet phase reactions.

With this limited data base it is premature to attempt to make conclusions about environmental factors which affect the relative importance of heterogeneous and gas phase chemical reactions. It is likely that relative humidity is an important factor since many aerosol species ($(NH_4)_2SO_4$, NH_4NO_3, NH_4HSO_4, NaCl, etc.) do not deliquesce until relative humidities exceed some critical value. Furthermore, ionic strengths of solutions decrease with increasing humidities, which would tend to increase the likelihood of droplet phase reactions at higher humidities.

It is interesting to note that aerosol formation in the Great Smoky Mountains, which apparently occurred as a result of droplet phase reactions, did not take place at night. This suggests the possibility that sunlight may also be a key ingredient in such reactions.

This analysis helps explain variations in submicron aerosol size distributions which have been observed in varied geographical settings. Data obtained in Tennessee and Alabama with the University of Minnesota Mobile Laboratories during the summer of 1978 (r.h. $\simeq$ 50–90%), for example, showed submicron volume distributions peaking at diameters of 0.3–0.5 μm. Data obtained in the southwestern United States during the summer of 1979 (r.h. $\simeq$ 5–20%), however, showed that submicron volume distributions tended to peak near 0.1 or 0.2 μm. This is consistent with the notion that droplet phase reactions (which favor growth of large particles) tend to be important in humid environments while condensational growth (which should lead to aerosols of smaller size) tends to be predominant in dry air.

Acknowledgements—This study was supported by U.S. Environmental Protection Agency grants No. R803851 and CR806801-01, W. E. Wilson, Jr., Project Officer. The contents of this paper do not necessarily reflect the views or policies of the Environmental Protection Agency.

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